

# (12) UK Patent Application (19) GB (11) 2 312 897 (13) A

(43) Date of A Publication 12.11.1997

(21) Application No 9708747.2	(51) INT CL <sup>6</sup> C09D 163/00 5/03
(22) Date of Filing 29.04.1997	
(30) Priority Data (31) 08644866 (32) 10.05.1996 (33) US	(52) UK CL (Edition O ) C3B BH B1D2B B1D2C B1D3 B1N1A B1N1X B1N4C B1N4F B1N4H B1N4J B1N4X B1N6D3 B1N6D6 B1N6D8 U1S S1392
(71) Applicant(s) <b>H B Fuller Company</b>  (incorporated in USA - Minnesota)  2900 Granada Lane, Oakdale, Minnesota 55128, United States of America	(56) Documents Cited GB 1529422 A JAPIO Abstract No:01299775 & JP590011375 A WPI Abstract Accession No: 82-20513E/198211 & JP570021465 A
(72) Inventor(s) Brian W Carlson Wayne G Eklund Christine M Giese	(58) Field of Search UK CL (Edition O ) C3B BEX BG BH , C3M MFP INT CL <sup>6</sup> C09D 5/00 5/03 ONLINE: CHABS, CLAIMS, JAPIO, RAPRA, WPI
(74) Agent and/or Address for Service <b>W P Thompson &amp; Co</b> Celcon House, 289-293 High Holborn, LONDON, WC1V 7HU, United Kingdom	

## (54) Catalyst for powder coatings

(57) A powder coating composition is prepared by combining components comprising an epoxy resin, a carboxylic acid-functional polyester compound, and a catalytic salt prepared from a mono- or di-carboxylic acid having at least one acid group with a pKa greater than about 2.9 and an amount of an imidazoline-based compound sufficient to react with the acid group having a pKa greater than about 2.9.

The epoxy resin may be derived from bisphenol A or triglycidyliscocyanurate.

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CATALYST FOR POWDER COATINGSField of Invention

5       The present invention relates to a powder coating composition. More particularly, this invention relates to a catalytic salt derived from a carboxylic acid and an amine for use in a powder coating composition.

Background of the Invention

10      Powder coating compositions are used in fusion-based coatings (i.e., coatings that are prepared by fusing or melting a powder to form a film). They are generally applied by conventional methods well known in the art in a thin layer to appropriate substrates. The individual powder particles are then heated to form a continuous melt coating on the substrate. Such heating is typically carried out in an  
15     oven or under heat or other sources of radiant energy. The melted material then cures to form an even coating.

Compared to other methods of coating substrates, powder coatings and the powder coating technology offer significant advantages. Powder coating compositions are essentially nonvolatile, generally nontoxic, and are solvent-free.  
20     Thus, there are generally no volatile organic compounds or other pollutants given off during preparation, application, or curing. Furthermore, coating processes using powder coating compositions generally produce very little waste because overspray powder can be collected and reused. Thus, in general, powder coatings are preferred to liquid-based coatings.

25      There are several systems of powder coatings that are known in the industry that are based on the reactions of epoxy-functional and acid-functional materials. These systems generally tend to require curing temperatures of about 175-200°C, and curing times of greater than about 20 minutes. In attempting to overcome this problem, acid/amine catalytic salts have been used as catalysts.  
30     Examples of such catalysts include the reaction product of imidazolines and various

carboxylic acids. However, not all such catalysts efficiently cure all systems. For example, the monosalts of the tri- and tetra-functional carboxylic acids generally only function as weak catalysts and do not generally allow rapid and complete cure at temperatures lower than about 175°C unless high levels of catalyst are used. An 5 example of such a system is set forth in Japanese Patent No. 57-21465 (Dainippon Ink Chemicals). In addition, systems which are catalyzed to cure rapidly often exhibit unacceptably low 20° and 60° gloss after cure. In particular, the 20° gloss is often much lower when compared to the uncatalyzed system.

There is therefore, generally, a need for a catalyst that is useful in the 10 reaction of acid-functional materials with epoxy-functional materials in powder coating systems, to provide substantially complete cure at a relatively low temperature in a relatively short period of time and which retains a relatively high percentage of 20° gloss when compared to an uncatalyzed system.

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#### Summary of the Invention

The present invention is based on the surprising catalytic effects found when using a specific group of catalytic salts of mono- and di-carboxylic acids and imidazolines. Advantageously and preferably, the amounts of catalyst used are typically at a lower level than that used in other systems and provide a 20 relatively high percentage of 20° gloss when compared to an uncatalyzed system.

The present invention can be described as a powder coating composition preparable by combining components comprising an epoxy-functional resin, a carboxylic acid-functional polyester compound, and a catalytic salt prepared from a mono- or di-carboxylic acid having at least one acid group with a pKa greater 25 than about 2.9 and an amount of an imidazole-based compound sufficient to react with the acid group having a pKa greater than about 2.9.

Detailed Description of the Invention

It has been discovered that relatively high gloss coatings can be prepared from the reaction of acid-functional polyesters with epoxy-functional compounds in a relatively short period of time at a relatively low temperature. This 5 results from the use of a catalytic salt prepared from a mono- or di-carboxylic acid having at least one acid group with a pKa greater than about 2.9 and an amount of an imidazoline-based compound sufficient to react with the acid group having a pKa greater than about 2.9.

10    Epoxy-Functional Compound

Epoxy-functional compounds suitable for preparing powder coatings have at least two epoxy groups per molecule and are solid at room temperature (i.e., 25-30°C). The epoxy compounds are, for example, solid epoxy resins based on bisphenol A (2,2'-bis(p-hydroxyphenyl)propane) and epichlorohydrin, i.e., the 15 diglycidyl ether of bisphenol A and higher addition products thereof. The equivalent weight of the solid epoxy resins based on bisphenol A are preferably 600-1500 and most preferably 650-725. Epoxy resins such as those known under the trade designations include "EPON" from Shell (Houston, TX) "ARALDITE" from Ciba-Geigy Corp. (Hawthorne, NY) and "DER" from Dow Chemical 20 (Midland, MI) are illustrative examples. Another suitable example is triglycidylisocyanurate (TGIC) from Ciba-Geigy under the trade designation of "ARALDITE PT-810." Although bisphenol A based solid epoxy resins, and TGIC are preferred, other suitable examples that can be used in combination with bisphenol A based solid epoxy resins, or TGIC, include solid epoxy resins based on 25 bisphenol F (4,4'-dihydroxydiphenylmethane), saturated bisphenol A (2,2'-bis(4-hydroxycyclohexyl)propane) and epichlorohydrin and higher addition products. Also included are epoxy resins made by the reaction of epichlorohydrin with a novolac resin. A novolac resin is a condensate of a phenol compound with formaldehyde in the presence of acid catalysts. The phenol compound can be

phenol itself, or such compounds as the cresols, xylenols, resorcinol, naphthols, and the like.

#### Carboxylic Acid-Functional Polyesters

5        Acid-functional compounds useful as co-reactants with the epoxy-functional compounds include acid-functional polyesters. These polyesters are prepared from polycarboxylic acids, their lower alkyl esters or anhydrides and polyhydroxylated compounds by methods already known per se, e.g., by esterification or interesterification, possibly in the presence of usual catalysts such  
10      as dibutyl-tin oxide or tetrabutyl titanate. Through a suitable choice of the reaction conditions and the COOH/OH ratio, these polyesters preferably have an acid number of about 20-80 mg KOH/g and are preferably practically free from hydroxyl groups, i.e., the hydroxyl number is less than about 15 mg KOH/g. They also have an average acid functionality of about 2-4. These polyesters preferably have a glass  
15      transition temperature ( $T_g$ ) of about 40-85°C, more preferably a  $T_g$  of about 45-75°C and most preferably a  $T_g$  of about 50-60°C. Examples include those known under the trade designation of "URALAC" from DSM (Augusta, GA), "CRYLCOAT" from UCB (Smyrna, GA), "RUCOTE" from Ruco Polymer (Hicksville, NY)

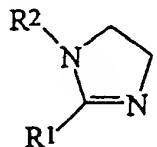
20      Suitable polycarboxylic acids useful for making this type of polyester include terephthalic acid, isophthalic acid, phthalic acid, trimellitic acid, pyromellitic acid, benzophenonetetracarboxylic acid, tetrahydrophthalic acid, hexahydroendomethylenetetrahydrophthalic acid, 1,3-cyclohexanedicarboxylic acid, 1,4-cyclohexanedicarboxylic acid, azelaic acid, adipic acid, succinic acid, glutaric acid, pimelic acid, suberic acid, sebacic acid, decanedicarboxylic acid, 25      dodecanddicarboxylic acid, maleic acid, etc., as well as, insofar as they are obtainable, from the corresponding anhydrides, acid chlorides or lower alkyl esters thereof.

Suitable polyhydroxylated compounds useful for making this type of polyester include ethylene glycol, propane-1,2-diol, propane-1,3-diol, butane-1,2-diol, 2,2-dimethylpropanediol-1,3 (neopentyl glycol), hexane-2,5-diol, hexane-1,6-diol, 2,2-[bis(4-hydroxycyclohexyl)]-propane, 1,4-dimethylocyclohexane, diethylene glycol, dipropylene glycol, and 2,2-bis[4-hydroxylethoxy]-phenylpropane and smaller amounts of polyols, such as glycerol, hexanetriol, pentaerythritol, sorbitol, trimethylolethane, trimethylolpropane and tris-(2-hydroxylethyl)-isocyanurate.

10 Catalytic salt

Mono- and Di-Carboxylic Acids - Monocarboxylic acids and dicarboxylic acids are compounds that have one and two carboxylic acid groups (-COOH) per molecule respectively. They include aromatic and aliphatic (saturated and unsaturated) acids or combinations thereof (i.e., araliphatic). Typical monocarboxylic acids or dicarboxylic acids include, but are not limited to, terephthalic acid, isophthalic acid, phthalic acid, benzoic acid, azelaic acid, adipic acid, succinic acid, glutaric acid, pimelic acid, suberic acid, sebacic acid, decanedicarboxylic acid, dodecandicarboxylic acid, acetic acid, 2-ethylhexanoic acid and maleic acid. The pKas of these acids are generally above 2.9. Further, the pKa of aromatic monoacids, the pKa of the second acid of aromatic dicarboxylic acids and the pKas of aliphatic (saturated and unsaturated) monocarboxylic acids and dicarboxylic acids are generally above 4.0.

Imidazolines - 2-Imidazolines may be represented by the following general structure:



25

wherein R<sup>1</sup> is hydrogen, an aromatic group, an aliphatic group (saturated or unsaturated), cycloaliphatic or an araliphatic group, preferably having about 1-12

carbon atoms. Examples include phenyl, 2-chlorophenyl, 2-hydroxyphenyl, 4-chlorophenyl, 4-methyl phenyl, and the like, alkyl, such as methyl, undecyl and the like, aralkyl, such as benzyl and the like, or hydrogen. R<sup>2</sup> is hydrogen or an alkyl group, preferably having about 1-12 carbon atoms, such as methyl and the like.

5 Representative 2-imidazolines include 2-phenyl-2-imidazoline, 2-(2-hydroxyphenyl)-2-imidazoline, 2-(2-chlorophenyl)-2-imidazoline, 2-(4-chlorophenyl)-2-imidazoline, 2-(4-methylphenyl)-2-imidazoline, 2-n-undecyl-2-imidazoline, 2-benzyl-2-imidazoline, 4,4-dimethyl-2-imidazoline, and 2-methyl-2-imidazoline.

10 The catalyst of the present invention includes reaction products (catalytic salts) of these imidazolines and mono- and di-carboxylic acids. The catalytic salts of these acids and imidazolines can be monosalts if the acid is a monocarboxylic acid, and monosalts or disalts if a dicarboxylic acid is used. To prepare a monosalt of a monocarboxylic acid or a dicarboxylic acid, equimolar  
15 amounts of the monocarboxylic acid or the dicarboxylic acid and the imidazoline are mixed, usually in a solvent. A solid salt is isolated by filtration followed by drying. A liquid salt can be isolated by removing the solvent. To prepare a disalt of a dicarboxylic acid, a 1:2 molar ratio of the dicarboxylic acid to the imidazoline is mixed, usually in a solvent. The salts can be isolated as discussed above.

20

#### Preparation of Coatings

The process of the preparation of a powder coating generally involves the blending of the solid materials, followed by extrusion through an extruder at about 75-110°C, grinding and sieving.

25 The powder-coating compositions of the invention can contain a variety of conventional ingredients including fillers, pigments, dyes, leveling agents, and other conventional additives. The fillers may be in the form of particles or fibers of compositions including ceramics, glass, silicone, quartz, mica, treated clay, calcium carbonate, calcium sulfate, barium sulfate, titanium dioxide, boron nitrides,

graphite, carbon black, glass fibers, asbestos fibers, metal powders, etc. The amount of filler depends upon the particular properties of the final coating desired.

The powder coating is then sprayed (usually by electrostatic spray techniques well known in the art) onto the substrate and cured by heating to a 5 specified temperature. These cured coatings are evaluated for a number of properties including forward and reverse impact resistance and 20° and 60° gloss.

The properties desired in a catalyst, are that the catalyst exhibit excellent latency (essentially no reactivity) during extrusion while exhibiting high reactivity at the cure temperature. Unfortunately, latency during extrusion is often 10 accompanied by only low reactivity at the cure temperature. As a result, if a catalyst is usable at all, it may need to be present in high amounts. It is generally desirable to use as little catalyst as possible to effect cure with the amounts preferably being no greater than about 2 parts per hundred parts of resin. Most preferably, 0.05-2 parts per hundred parts of resin are used. In addition, although some decrease in 15 physical properties may be tolerated, as much retention of these properties (like gloss) as is possible is desired. Therefore, a desirable catalyst exhibits high latency, high reactivity at acceptable cure temperatures, and good retention of gloss.

There are a number of properties which are important in a cured powder coating. These properties generally relate to appearance and performance. 20 A very important performance property is the forward and reverse impact resistance of the cured coating. In general, a flexible coating is considered to have reached its ultimate impact and achieved full cure when 160 in-lbs (1.84 kg-m) of forward and reverse impact are reached. This test (ASTM D2794-93 using a 0.625 in (15.9 mm) punch) is very well known by those skilled in the art. A very important appearance 25 criteria is the gloss of the cured coating. For many coatings, it is important to have as high a gloss as possible. Those skilled in the art are very familiar with the measurement of 60° and 20° gloss. In general, the 60° gloss where the incident light beam is reflected from the cured coating at a 60° angle, although widely used, is a less discriminating test than 20° gloss. The 20° gloss measures the incident light

beam reflected from the cured coating at a 20° angle. The 20° gloss result is indicative of the smoothness of the cured coating.

It is therefore highly desirable to achieve a high level of gloss and 160 in-lbs (1.84 kg-m) of forward and reverse impact. However, a third parameter  
5 is the amount of time it takes to achieve 160 in-lbs (1.84 kg-m) of forward and reverse impact. It is generally observed that a slow cure results in a high gloss while a fast cure results in lower gloss. In many cases, a fast cure speed at a given temperature while maintaining a high gloss is highly desired. Therefore, the challenge is to find a catalyst which can quickly cure a powder coating at a given  
10 temperature while maintaining a high level of gloss. In evaluating catalysts, it is extremely important to compare catalysts at the same cure speed. An inefficient catalyst which results in a relatively slow cure can have a higher gloss than the same level of an efficient catalyst which results in a relatively fast cure. As a result, the levels of the catalysts must be adjusted so that equivalent cure speeds at equivalent  
15 temperatures are obtained.

The time to 160 in-lbs (1.84 kg-m) of forward and reverse impact is used as the measure of the cure speed of a powder coating. Systems without any catalyst were evaluated first to get baseline readings for the time it took to achieve this impact value. A significantly shorter time to 160 in-lbs (1.84 kg-m) of impact  
20 was then chosen as the cure speed for evaluation of the catalytic salts.

#### Test Method for Selection of Catalytic Salts

"Model Composition A" for powder coatings based on acid-terminated polyesters and solid bisphenol A based epoxy resins - A powder is prepared when 50 parts of  
25 "CRYLCOAT 340", an acid-terminated polyester available from UCB (Smyrna, GA); 50 parts "ARALDITE GT-7013", a solid bisphenol A based epoxy resin available from Ciba-Geigy (Hawthorne, NY); 1.5 parts "RESIFLOW P-67", an acrylic flow modifier available from ESTRON Chemical (Calvert City, KY); a catalytic salt; and 75 parts "RCL-2", titanium dioxide available from SCM Chemical, Inc.

(Baltimore, MD) are bag blended and extruded and 0.2% of "ALUMINUM OXIDE C", aluminum oxide from Degussa (Ridgefield Park, NJ) is post-blended followed by grinding and sieving through a 140 mesh sieve to give a powder coating which could be electrostatically sprayed.

5           The powder coating composition as described above without the catalytic salt is defined as Control A.

The powder is sprayed onto 0.5 mm x 76 mm x 127 mm smooth, cold rolled steel panels so that the coating thickness after cure would be  $50 \pm 5.0$  microns. The panels are then cured for varying times in a forced air oven. Tests are  
10 conducted for the amount of time it took at a given temperature ( $149^{\circ}\text{C}$ ) to achieve 160 in-lbs (1.84 kg-m) of forward and reverse impact per ASTM D2794-93 using a 0.625 in (15.9 mm) punch. The catalyst level is adjusted so that the time to achieve this level of impact is 9-10 minutes for the cures at  $149^{\circ}\text{C}$ . Once again, the  
15 thickness of the cured coatings is  $50 \pm 5.0$  microns on 0.5 mm x 76 mm x 127 mm smooth cold rolled steel panels. The  $20^{\circ}$  and  $60^{\circ}$  glosses are then measured for the cured coatings. When the ratio of the  $20^{\circ}$  gloss of the cured coating to the  $20^{\circ}$  gloss of Control A cured to 160 in-lbs (1.84 kg-m) of forward and reverse impact on 0.5 mm x 76 mm x 127 mm cold rolled steel at  $149^{\circ}\text{C}$  with a cured film thickness of  $50 \pm 5$  microns is greater than about 50%, the catalyst is acceptable. This ratio of the  
20  $20^{\circ}$  glosses is defined as the normalized  $20^{\circ}$  gloss using Model Composition A.

"Model Composition B" for powder coatings based on acid-terminated polyesters and triglycidylisocyanurate - A powder is prepared when 93 parts of "CRYLCOAT 440", an acid-terminated polyester available from UCB (Smyrna, GA); 7 parts  
25 "ARALDITE PT-810", TGIC available from Ciba-Geigy (Hawthorne, NY); 1.5 parts "RESIFLOW P-67", an acrylic flow modifier available from ESTRON Chemical (Calvert City, KY); 1.0 parts "URAFLOW B", benzoin available from ESTRON Chemical (Calvert City, KY); a catalytic salt; and 75 parts "RCL-2", titanium dioxide available from SCM Chemical, Inc. (Baltimore, MD) are bag blended and

extruded and 0.2% of "ALUMINUM OXIDE C", aluminum oxide from Degussa (Ridgefield Park, NJ) is post-blended followed by grinding and sieving through a 140 mesh sieve to give a powder coating which could be electrostatically sprayed.

The powder coating composition as described above without the  
5 catalytic salt is defined as Control B.

The powder is sprayed onto 0.5 mm x 76 mm x 127 mm smooth,  
cold rolled steel panels so that the coating thickness after cure would be 50 ± 5.0  
microns. The panels are then cured for varying times in a forced air oven. Tests are  
conducted for the amount of time it took at a given temperature (149°C) to achieve  
10 160 in-lbs (1.84 kg-m) of forward and reverse impact per ASTM D2794-93 using a  
0.625 in (15.9 mm) punch. The catalyst level is adjusted so that the time to achieve  
this level of impact was 18-20 minutes for the cures at 149°C. Once again, the  
thickness of the cured coatings is 50 ± 5.0 microns on 0.5 mm x 76 mm x 127 mm  
smooth cold rolled steel panels. The 20° and 60° glosses are then measured for the  
15 cured coatings. When the ratio of the 20° gloss of the cured coating to the 20° gloss  
of Control B cured to 160 in-lbs (1.84 kg-m) of forward and reverse impact on 0.5  
mm x 76 mm x 127 mm cold rolled steel at 149°C with a cured film thickness of 50  
± 5 microns is greater than about 70%, the catalyst is acceptable. This ratio of the  
20° glosses is defined as the normalized 20° gloss using Model Composition B.

20 The normalized gloss criteria are different for Model Composition A  
and Model Composition B due to the inherent difference in reactivity between the  
two systems. In general, if a system has a lower reactivity it will have higher gloss.  
As a result, the inherently slower Model Composition B has a higher normalized  
gloss.

25 It is surprising that the monosalts of aromatic monocarboxylic acids,  
the monosalts and disalts of aromatic dicarboxylic acids, the monosalts of saturated  
monocarboxylic acids, and the monosalts and disalts of saturated aliphatic  
dicarboxylic acids were able to retain much higher levels of normalized 20° gloss  
using Model Composition A than salts of trifunctional and tetrafunctional aromatic

acids and cycloaliphatic acids. These preferably have a normalized 20° gloss of at least 50%, more preferably a normalized 20° gloss of greater than about 60%, and most preferably a normalized 20° gloss of greater than about 70%.

Further, disalts of aromatic dicarboxylic acids, the monosalts of aromatic monocarboxylic acids, the monosalts of saturated aliphatic monocarboxylic acids and the monosalts and disalts of aliphatic (saturated and unsaturated) dicarboxylic acids were able to retain much higher levels of normalized 20° gloss using Model Composition B than salts of trifunctional and tetrafunctional aromatic acids and cycloaliphatic acids and monosalts of aromatic dicarboxylic acids. These preferably have a normalized 20° gloss of at least 70%, more preferably a normalized 20° gloss of greater than about 80%, and most preferably a normalized 20° gloss of greater than about 90%.

In both systems, when catalysts were adjusted to achieve the same cure speed, there were surprising differences in the ability of the catalysts to retain high levels of normalized 20° gloss. These differences define which catalysts are useful for the preparation of powder coatings having high gloss and those which are not suitable for this purpose.

Alternatively, the imidazoline compound itself can be used as a catalyst for the reaction of the epoxy-functional compound and the acid-functional polyester.

The following non-limiting examples are offered to further illustrate the various specific and preferred embodiments and techniques. It should be understood, however, that many variations and modifications may be made while remaining within the scope of the present invention.

Experimental ExamplesTest Method

The test method measures the reactivity and gloss properties of a powder coating prepared according to the method of the present invention. The powder material is sprayed to provide a cured coating with a thickness of  $50 \pm 5$  microns (about  $2.0 \pm 0.2$  mils) on a  $0.5 \text{ mm} \times 76 \text{ mm} \times 127 \text{ mm}$  smooth cold rolled steel panel. Panels are cured in a forced air oven at various temperatures with forward and reverse impact being measured using a Gardner Impact Tester per ASTM D2794-93 using a 0.625 in (15.9 mm) punch. The shortest time at which the coating achieves 160 in-lbs (1.84 kg-m) of forward and reverse impact is recorded.

The  $20^\circ$  and  $60^\circ$  glosses for the cured coatings on  $0.5 \text{ mm} \times 76 \text{ mm} \times 127 \text{ mm}$  smooth cold rolled steel panels at a cured film thickness of about  $50 \pm 5.0$  microns are measured using a Gardner Haze-Gloss Meter. These glosses and the normalized  $20^\circ$  gloss are recorded.

Example 1Preparation of the Dodecanedioic Acid/2-Phenylimidazoline Disalt

For the general preparation of the catalytic salts, the factors which were varied were: ratio of acid groups to 2-phenylimidazoline (monosalt or disalt); solvent; percent solids during the reaction; temperature of 2-phenylimidazoline addition; temperature at which the reaction was held; and time for which the reaction was held.

With trimellitic acid, the monosalt with 2-methylimidazoline was made. The 2-ethylhexanoic acid/2-phenylimidazoline salt was a liquid and was isolated by rotary evaporation of the solvent. The 2-phenylimidazoline disalt with pyromellitic acid is a commercial product called "VESTAGON B-55" from Hüls (Piscataway, NJ). The 2-phenylimidazoline monosalt with pyromellitic acid is a

commercial product called "VESTAGON B-68" also from Huels (Piscataway, NJ). Both products were used as received.

22.0 g of "CORFREE M-2" (dodecanedioic acid, 0.0955 moles, from E.I. DuPont (Wilmington, DE)) was added to 100 g of methylethylketone (MEK) at room temperature. The temperature was raised to 70°C and 28.0 g of "VESTAGON B-31" (2-phenylimidazoline, 0.1915 moles from Huels (Piscataway, NJ)) were added over 30 minutes. The temperature was held at 70°C for 1.5 hours. The slurry was cooled to near room temperature, filtered and dried.

Table 1

Catalytic salts made with 2-phenylimidazole (B-31)

Acid Used in Catalytic Salt Preparation	Monosalt/ Disalt	% Solids During Reaction	Solvent	Temp. in °C of 2- Phenylimida- zoline Addition	Hold Time (hrs)	Hold Temp in °C
Benzophenone Tetracarboxylic Acid	Mono	25%	MEK	70	1	70
Trimellitic Acid*	Mono	33%	IPA	70	1	70
Terephthalic Acid	Mono	40%	IPA	78	3	78
Isophthalic Acid	Mono	25%	IPA	78	1	78
Isophthalic Acid	Di	25%	IPA	78	no hold	---
Benzoic Acid	Mono	33%	MEK	75	no hold	---
Adipic Acid	Mono	40%	IPA	78	no hold	---
Dodecanedioic Acid	Mono	33%	IPA	78	no hold	---
Dodecanedioic Acid	Di	33%	MEK	70	1.5	78
Sebacic Acid	Mono	33%	MEK	75	1	75
Sebacic Acid	Di	33%	MEK	70	4	70
1,4 - Cyclohexanedicarboxylic Acid	Mono	33%	IPA	70	0.5	70

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2-Ethylhexanoic Acid**	Mono	33%	IPA	70	no hold	---
Maleic Acid	Mono	25%	MEK	70	1	70
Maleic Acid	Di	33%	IPA	50	0.5	60

\* Salt with 2-methylimidazoline

\*\* Liquid salt which was isolated by rotary evaporation

MEK = Methylethylketone

IPA = Isopropanol

Example 2Procedure for Preparing Coatings Using Acid-Terminated Polyester and Triglycidylisocyanurate (TGIC)

A powder material is produced when 93 parts "CRYLCOAT 440",  
5 an acid-terminated polyester available from UCB (Smyrna, GA); 7 parts  
"ARALDITE PT-810", TGIC available from Ciba-Geigy (Hawthorne, NY); 1.5  
parts "RESIFLOW P-67", an acrylic flow modifier available from Estron Chemical  
(Calvert City, KY); 1.0 parts "URAFLOW B", benzoin available from Estron  
Chemical (Calvert City, KY); a catalytic salt; and 75 parts "RCL-2", titanium  
10 dioxide available from SCM Chemical, Inc. (Baltimore, MD) were bag blended and  
extruded and 0.2% of "ALUMINUM OXIDE C", aluminum oxide available from  
Degussa (Ridgefield Park, NJ) was post-blended followed by grinding and sieving  
through a 140 mesh sieve to give a powder coating which could be electrostatically  
sprayed.

15 The powder was sprayed onto 0.5 mm x 76 mm x 127 mm smooth,  
cold rolled steel panels so that the coating thickness after cure would be  $50 \pm 5.0$   
microns. The panels were then cured for varying times in a forced air oven. Tests  
were conducted for the amount of time it took at a given temperature ( $149^{\circ}\text{C}$ ) for the  
coating to achieve 160 in-lbs (1.84 kg-m) of forward and reverse impact. The  
20 catalytic salt level was adjusted so that the time to achieve this level of impact was  
19-20 minutes for the cures at  $149^{\circ}\text{C}$ . Once again, the thickness of the cured  
coatings was  $50 \pm 5.0$  microns on 0.5 mm x 76 mm x 127 mm smooth cold rolled  
steel panels. The  $20^{\circ}$  and  $60^{\circ}$  glosses were then measured for the cured coatings and  
the normalized  $20^{\circ}$  gloss using Model Composition B was calculated. Even high  
25 levels of catalytic salts based on pyromellitic acid and trimellitic acid were unable to  
achieve 160 in-lbs (1.84 kg-m) at forward and reverse impact in 20 minutes or less  
using a cure temperature of  $149^{\circ}\text{C}$ .

The results were recorded as follows: catalytic salt level in phr (parts per hundred parts of resin of "CRYLCOAT 440" acid-terminated polyester plus PT-

810 TGIC); cure time to 160 in-lbs (1.84 kg-m) of forward and reverse impact; 20° and 60° glosses; and normalized 20° gloss using Model Composition B.

The abbreviations used in Tables 2 and 3 are as follows:

5

PMA	Pyromellitic Acid	Aromatic Tetrafunctional Acid
BTA	Benzophenone Tetracarboxylic Acid	Aromatic Tetrafunctional Acid
TMA	Trimellitic Acid	Aromatic Trifunctional Acid
TPA	Terephthalic Acid	Aromatic Diacid
PIA	Isophthalic Acid	Aromatic Diacid
Benzoic	Benzoic Acid	Aromatic Monoacid
Adipic	Adipic Acid	Aliphatic Diacid
DDA	Dodecanedioic Acid	Aliphatic Diacid
Sebacic	Sebacic Acid	Aliphatic Diacid
CHDA	1,4 - Cyclohexanedicarboxylic Acid	Cycloaliphatic Diacid
2-EH	2-Ethylhexanoic Acid	Aliphatic Monoacid
Maleic	Maleic Acid	Unsaturated Aliphatic Diacid
B31	2-Phenylimidazoline	Imidazoline
2MIZ	2-Methylimidazoline	Imidazoline

Table 2

## 149°C Cures of Acid-Terminated Polyesters and TGIC

Salt Type	phr	Time to 160 in-lbs (1.84 kg-m) of impact at 149°C	Gloss 20°/60°	Normalized 20° Gloss using Model Composition B
None (Control B)	—	65	39/42	100
B31*	0.3	19	23/56	59
PMA/B31 Mono	10.0	35	20/49	51
PMA/B31 Di	6.0	23	22/41	56
BTA/B31 Mono	3.0	20	25/46	64
TMA/2MIZ Mono	3.0	24	20/39	51
TPA/B31 Mono	1.0	20	25/45	64
PIA/B31 Mono	1.0	20	25/44	64
PIA/B31 Di	0.3	18	38/52	97
Benzoic/B31	0.3	20	38/56	97
Adipic/B31 Mono	0.4	20	36/46	92
DDA/B31 Mono	0.5	19	43/61	110
DDA/B31 Di	0.35	20	38/51	97
Sebacic/B31 Mono	0.4	20	39/57	100
Sebacic/B31 Di	0.3	20	36/46	92
CHDA/B31 Mono	0.75	19	20/51	51

2-EH/B31 Mono	0.45	20	36/48	92
Maleic/B31 Mono	0.45	20	36/47	92
Maleic/B31 Di	0.4	20	36/44	92

\* 2-Phenylimidazoline, not a salt

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### Example 3

#### Procedure for Preparing Coatings Using Acid-Terminated Polyester and Solid Bisphenol A Based Epoxy

A powder material is produced when 50 parts "CRYLCOAT 340", an acid-terminated polyester available from UCB (Smyrna, GA); 50 parts 10 "ARALDITE GT-7013", a solid bisphenol A based epoxy resin available from Ciba-Geigy (Hawthorne, NY); 1.5 parts "RESIFLOW P-67", an acrylic flow modifier available from ESTRON Chemical (Calvert City, KY); a catalytic salt; and 75 parts "RCL-2", titanium dioxide available from SCM Chemical, Inc. (Baltimore, MD) were bag blended and extruded and 0.2% of "ALUMINUM OXIDE C", 15 aluminum oxide available from Degussa (Ridgefield Park, NJ) was post-blended followed by grinding and sieving through a 140 mesh sieve to give a powder coating which could be electrostatically sprayed.

Powder was sprayed onto 0.5 mm x 76 mm x 127 mm smooth, cold 20 rolled steel panels so that the coating thickness after cure would be 50 ± 5.0 microns. The panels were then cured for varying times in a forced air oven. Tests were conducted for the amount of time it took at a given temperature (149°C) for the coating to achieve 160 in-lbs (1.84 kg-m) of forward and reverse impact. The catalytic salt level was adjusted so that the time to achieve this level of impact was 25 9-10 minutes for the cures at 149°C. Once again, the thickness of the cured coatings was 50 ± 5.0 microns on 0.5 mm x 76 mm x 127 mm smooth cold rolled

steel panels. The 20° and 60° glosses were then measured for the cured coatings and the normalized 20° gloss using Model Composition A was calculated.

The results were recorded as follows: catalytic salt level in phr (parts per hundred parts of resin of "CRYLCOAT 340", acid-terminated polyester plus 5 "ARALDITE GT-7013" solid bisphenol A based epoxy); cure time to 160 in-lbs (1.84 kg-m) of forward and reverse impact; 20° and 60° glosses; and normalized 20° gloss using Model Composition A.

**Table 3**  
10    **149°C Cures of Acid Terminated Polyesters and Solid Bisphenol A Based Epoxies**

Salt Type	phr	Time to 160 in-lbs (1.84 kg-m) of impact at 149°C Cure Time (Min)	Gloss 20°/60°	Normalized 20° Gloss using Model Composition A
None (Control A)	—	23	85/99	100
B31*	0.6	10	45/94	53
PMA/B31 Mono	10.0	10	41/90	48
PMA/B31 Di	5.0	10	41/92	48
BTA/B31 Mono	4.0	10	38/89	45
TMA/2MIZ Mono	5.0	10	35/87	41
TPA/B31 Mono	1.25	10	63/99	74
PIA/B31 Mono	1.5	10	63/98	76
PIA/B31 Di	0.75	10	64/98	74
Benzoic/B31	1.0	10	60/98	71

Adipic/B31 Mono	1.0	10	72/100	85
DDA/B31 Mono	1.25	10	60/98	71
DDA/B31 Di	0.75	10	67/100	79
Sebacic/B31 Mono	1.25	9	61/98	72
Sebacic/B31 Di	0.6	9	64/99	75
CHDA/B31 Mono	1.75	10	30/84	35
2-EH/B31 Mono	1.25	10	64/99	75

\* 2-Phenylimidazoline, not a salt

The complete disclosures of all patents, patent documents, and  
 5 publications cited herein are incorporated by reference as if individually  
 incorporated. The foregoing detailed description and examples have been given for  
 clarity of understanding only. No unnecessary limitations are to be understood  
 therefrom. The invention is not limited to the exact details shown and described, for  
 variations obvious to one skilled in the art will be included within the invention  
 10 defined by the claims.

WHAT IS CLAIMED IS:

1. A powder coating composition comprising:
  - (a) an epoxy-functional resin;
  - (b) a carboxylic acid-functional polyester compound; and
  - (c) a catalytic salt prepared from a mono- or di-carboxylic acid having at least one acid group with a pKa greater than about 2.9 and an amount of an imidazoline-based compound sufficient to react with the acid group having a pKa greater than about 2.9.
2. A powder coating composition comprising a mixture of:
  - (a) an epoxy functional resin;
  - (b) a carboxylic acid-functional polyester compound; and
  - (c) a catalytic salt prepared from a mono- or di-carboxylic acid having at least one acid group with a pKa greater than about 2.9 and an amount of an imidazoline-based compound sufficient to react with the acid group having a pKa greater than about 2.9.
3. The powder coating composition of Claim 1 or 2 wherein the epoxy has at least two epoxy groups per molecule.
4. The powder coating composition of Claim 3 wherein the epoxy resin is triglycidylisocyanurate.
5. The powder coating composition as any of Claims 1 to 4 wherein the carboxylic acid-functional polyester has an acid number of about 20-80 mg KOH/g and a hydroxyl number that is less than about 15 mg KOH/g.
6. The powder coating composition of any of the preceding claims wherein the carboxylic acid-functional polyester has an average acid functionality of about 2-4 and a glass transition temperature ( $T_g$ ) of about 40-85°C.
7. The powder coating composition of Claim 6 wherein the carboxylic acid-functional polyester has a glass transition temperature ( $T_g$ ) of about 50-60°C.

8. A coating prepared from a powder coating composition of any of the preceding claims wherein the catalytic salt is selected to provide a normalized 20° gloss that is greater than about 50% in a Model Composition A.
9. The powder coating composition of Claim 8 wherein the catalytic salt is selected to provide a normalized 20° gloss that is greater than about 60% in a Model Composition A.
10. A method of preparing a coating comprising:
  - (a) applying a coating composition as in any of Claims 1-7 onto at least one surface of a substrate;
  - (b) heating said substrate bearing said coating composition to a temperature of less than about 210°C for less than about 30 minutes.



Patent  
Office

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Application No: GB 9708747.2

Examiner:

Miss Maureen M.  
Kelman  
9 July 1997

Claims searched: 1 to 10

Date of search:

**Patents Act 1977**  
**Search Report under Section 17**

**Databases searched:**

UK Patent Office collections, including GB, EP, WO & US patent specifications, in:

UK Cl (Ed.O): C3B BEX BG BH, C3M MFP

Int Cl (Ed.6): C09D 5/00, 5/03

Other: ONLINE: CHABS, CLAIMS, JAPIO, RAPRA, WPI

**Documents considered to be relevant:**

Category	Identity of document and relevant passage	Relevant to claims
Y	GB 1529422 A LABOFINA see the claims and Examples	1 to 10
Y	JAPIO Abstract No: 01299775 & JP590011375 A (NIPPON ESTER) 20 January 1984 see abstract	1 to 10
Y	WPI Abstract Accession No: 82-20513E/198211 & JP570021465 A (DAINIPPON INK) 04 February 1982 see abstract	1 to 10

X Document indicating lack of novelty or inventive step	A Document indicating technological background and/or state of the art.
Y Document indicating lack of inventive step if combined with one or more other documents of same category.	P Document published on or after the declared priority date but before the filing date of this invention.
& Member of the same patent family	E Patent document published on or after, but with priority date earlier than, the filing date of this application.